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Extraction of selected metals from spent hydrodesulfurization catalyst using alkali leaching agent

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ABSTRACT

The aim of present study is to examine the dissolution and kinetics of valuable metals from spent hydrodesulfurization catalyst using potassium hydroxide. Due to low solubility of metal oxides of Ni and Co in alkali medium, only the recovery of Mo and Al was investigated. Optimum roasting temperature and time were determined 600°C and 60 min., respectively. The maximum dissolution yields of Mo (83.54%) and Al (36.89%) were reached under optimum leaching conditions. The leaching behavior of both metals is represented by the shrinking core model and liquid film diffusion is controlled the process. Activation energies found to be 14.71 kJ/mol and 17.84 kJ/mol for Mo and Al, respectively.

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leaching; kinetic



Introduction

The solid catalysts with high selectivity using in hydrocarbon conversions are widely used to increase the process efficiency in the petroleum refinery plants.^[1–3] These catalysts have a heterogeneous structure due to the presence of various metal oxides and metal sulfides.^[4] They are called the spent hydrodesulfurization (HDS) catalyst due to deactivate with metal fouling following the hydro-treatment process and it causes a large scale of solid waste problem in petroleum refineries.^[5–10] The amount of the spent HDS catalyst is estimated to be approximately 150,000–170,000 tons/year in the worldwide. Also, it is classified as hazardous waste because of high metal sulfur/oxide content.^[10–12] The assessment of these wastes is an important in terms of human and environmental health as well as economically.

There are different applications toward the valorization of the spent HDS catalyst; landfilling, regeneration, recovery of precious metals in the catalyst structure.^[13] The landfilling is not preferred due to the laws and regulations related to the environment are very strict and the large landfill area requirement.^[5,7] The regeneration is not preferred because it is not available for oil refineries and can be performed for a limited number of cycles.^[14] Also, it is not possible to regenerate the spent HDS catalysts that lost their activity in thermal decomposition and phase separation processes.^[15] On

the other hand, it is known that the spent HDS catalysts were evaluated as secondary metal sources due to the precious metals (Co, Ni, Mo and Al *etc.*) in their content.^[5,6,16,17] Nowadays, the recovery of precious metals from the spent HDS catalysts is carried out by two different methods; hydrometallurgical and pyrometallurgical processes.^[18,19]

Hydrometallurgical method is an effective, safely, low-cost and eco-friendly process commonly used to recover precious metals from secondary metal sources such as the spent HDS catalyst in recent years.^[20,21] Numerous studies related to leaching of the spent HDS catalysts have been performed in the presence of various leaching agents; sulfuric acid^[22,23], hydrochloric acid^[24], citric acid^[25], tartaric acid^[26], ammonia^[27], ammonium hydroxide, and ammonium carbonate.^[28] Also, alkali leaching agents are used alternatively to the aforementioned above chemical compounds. They are selective especially for vanadium and molybdenum metals, and usually cause undesirable impurities such as silica to pass into solution.^[29] On the other hand, since the spent HDS catalysts are used to remove sulfur from petroleum, they contain excessive amounts of organic pollutants and cannot be directly subjected to leaching.^[19] Therefore, pyrometallurgical pre-treatments such as oxidation and roasting are applied to the spent HDS catalyst to ensure that precious metals are passed into the solution with high efficiency.^[5,6,30–33]

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There are extensive studies on combination of hydro- and pyro-metallurgical processes for recovery metals from the spent HDS catalysts in the literature; however, the number of studies carried out in the presence of alkaline reactants is limited. The aim of the present paper is to examine the leaching behaviors and affecting parameters on the leaching process in the presence of KOH as an alkali leaching agent. Furthermore, the dissolution kinetics were analyzed based on heterogeneous reaction models and the most suitable model for experimental data was determined.

Experimental studies

Characterization of materials

The spent HDS catalyst was provided from a petroleum refinery in Romania. In the experiments, KOH in analytical purity was used as the alkali leaching reagent. The spent HDS catalyst was crushed, grounded and sieved to achieve the desired particle size, respectively. The particle size distribution of the powder samples was analyzed as shown in Fig. 1 (Malvern, Mastersizer 3000). Fifty percent and 90% of the particles have a particle size smaller than 24.8 μm and 63.3 μm , respectively. The powder samples were dried at 105°C and then stored in plastic bottles for subsequent leaching experiments. As seen from Table 1, metal content of the spent HDS catalyst was determined by microwave dissolving treatment. Then, the powder samples were roasted in air medium at different roasting temperatures and times using chamber furnace at a heating rate of 10°C/min.

The surface morphologies and elemental contents of the unroasted, roasted and alkali leached residue catalysts were characterized by SEM-EDX analysis. According to results in Fig. 2, the spent HDS catalyst

Table 1. Metal content of the spent Mo-Co-Ni/Al₂O₃ catalyst.

Components (wt.%)								
Al	Mo	Co	Ni	Ca	Fe	C	S	P
36.85	8.57	1.92	1.87	0.49	0.024	14.02	0.68	0.36

contains Mo, Co, Ni, and Al before roasting treatment, SO₂ and CO₂ gases are output from the structure depending on the temperature after the roasting process, and it is rich in terms of metal content. On the other hand, roasting and leaching process were caused an increase in surface area and also a decrease in pore volume as seen from Table 2.

The phase analysis was performed by X-ray diffraction (Rigaku, SmartLab). The XRD patterns of unroasted spent HDS catalyst is illustrated in Fig. 3. Its structure is quite complex and amorphous. In addition, it is seen that the main characteristic peaks belong to metal oxide compounds (CoO, MoO₂, Al₂O₃, NiO and Ni₂O₃).

Leaching tests

All leaching studies were conducted in 500 ml. erlenmeyer flasks using a shaker incubator (Zhcheng ZHWY-200D) adjustable the temperature and stirring speed (Mtops HSD180). The leaching solutions (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 M) were prepared using KOH. Then, the solution temperatures have been adjusted, the samples are added, stirred for the desired reaction time and filtered, respectively. Finally, the metal extraction yields were analyzed by an atomic absorption spectrophotometer (Perkin Elmer AAnalyst-400) and ICP-MS (Agilent 7500ce Octopole). Leaching experiments were performed in triplicate and all results are presented as mean values with standard deviations. The flow diagram

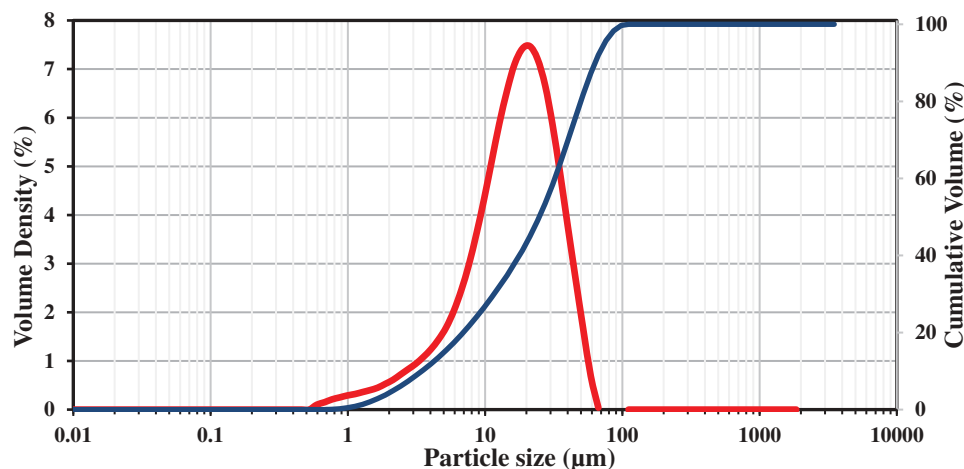


Figure 1. Particle size distribution of the unroasted spent HDS catalyst.

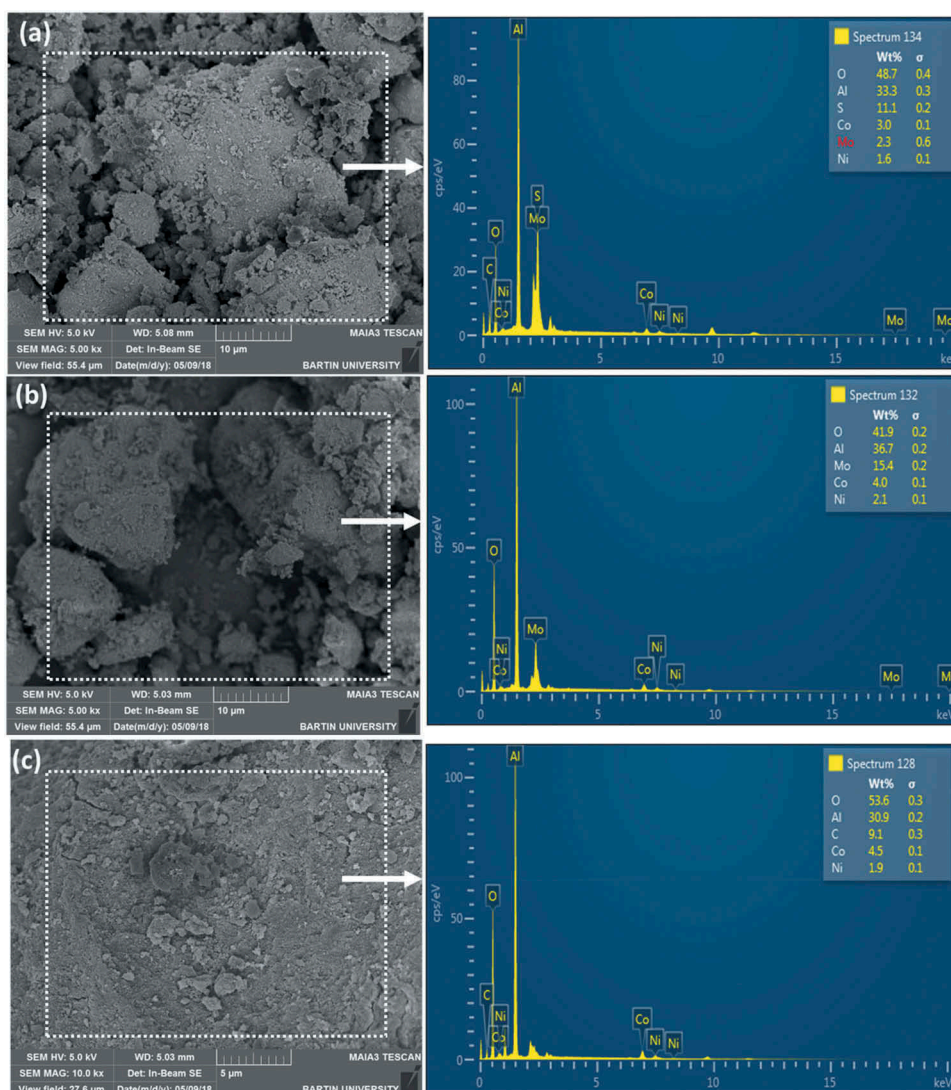


Figure 2. SEM images of unroasted (a), roasted (b) and leached catalyst (c).

Table 2. Values of surface area and pore volume of the spent HDS catalyst.

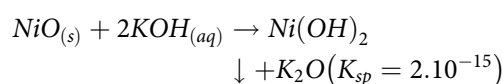
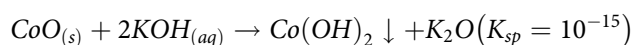
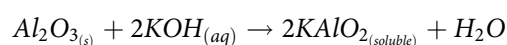
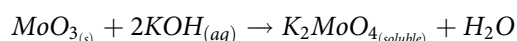
Sample	Surface area (m ² /g)	Pore volume (ml/g)
Unroasted catalyst	148.9	0.97
Roasted catalyst	259.9	0.36
Leached catalyst	315.8	0.18

of the roasting and alkali leaching process is given in Fig. 4.

Dissolution and precipitation reactions

It is known that all the metals in the spent HDS catalyst structure are dissolved in a certain amount in the acidic medium.^[34,35] Also, some metals such as Mo, Al, Ni, and Co were partially dissolved in the presence of alkali leaching agent.^[36] For this study, dissolution and

precipitation reactions between KOH and the spent catalyst can be written as follows^[37];



Since Mo and Al metals are amphoteric, they are readily soluble in both acidic and basic leaching mediums. However, Co and Ni are only dissolved in the acidic conditions. Leaching experiments were performed at low KOH concentrations (0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 M) and at pH range of 10.5–11. Therefore, the solubility of Mo and Al is high while the solubility of Co and Ni is quite low for these leaching conditions as

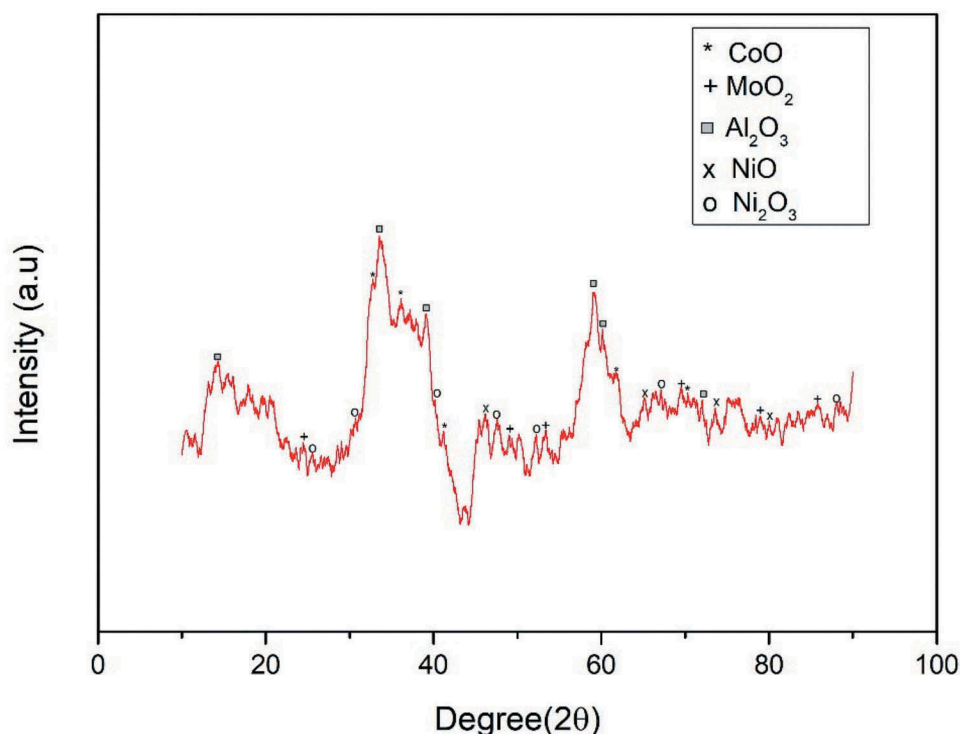


Figure 3. XRD patterns of the roasted spent HDS catalyst.

above-mentioned in the reactions.^[30,38] For this reason, the amounts of Mo and Al passing into the solution were investigated in this study.

Result and discussion

Effect of roasting temperature and time

The metal sulfides formed in the catalyst structure after the petroleum refining process converted into easily soluble metal oxide form by the roasting treatment. With the roasting process, carbon and sulfite are removed from the catalyst structure and the weight loss occurs. The prepared spent HDS catalyst powders were roasted at different temperatures (200–800°C) and times (10–240 min.) and then leaching experiments were performed. According to the results in Figs. 5 and 6, a raise in roasting temperature and time was resulted in an increase in metal extraction efficiencies. The optimum roasting temperature was set at 600°C to both reach high metal extraction values and to avoid formation of complex metal oxides at higher temperatures.^[19] Similarly, roasting time was chosen 60 min. After 60 min. at 600°C, the metal extraction yield was considered stable since the increase rate in further dissolution percentages was quite a little. In conclusion, the maximum dissolution percentages of Mo and Al were determined to be 81.95% and 33.82%, respectively.

Effect of particle size

The particle size was varied from +1200–600 μm to +30–20 μm to evaluate the effect of particle size on both metals dissolution. In terms of Fig. 7, the increase of the particle size was influenced negatively the leaching efficiency and a decrease was observed in the metal extraction yield. The highest metal dissolution percentages for Mo and Al were found 82.65% and 34.11%, respectively. On the other hand, there is no notable difference in dissolution amounts of both metals when the particle size is less than +150–75 μm as shown in Fig. 6. It may be attributed to metals liberation in spent HDS catalyst and effectively exposure to the alkali leaching agent.^[39]

Effect of liquid to solid ratio

The experiments were performed at various L/S ratios (2.5–25 ml/g) to investigate the effect of liquid to solid ratio on dissolution rates of metals. The results in Fig. 8 exhibit that the leaching yields of both metals increases with a raise in the L/S ratio. The maximum recovery values of Mo (94.75%) and Al (44.28%) were obtained at 15 L/S ratio and remained stable as the L/S ratio is increased from 15 to 25 ml/g. This is due to the limitation of the recovery efficiency of metals within the spent HDS catalyst because of the lack of enough leaching agent in solution medium.^[39] The optimum liquid-to-solid ratio was selected 15 ml/g for further experiments.

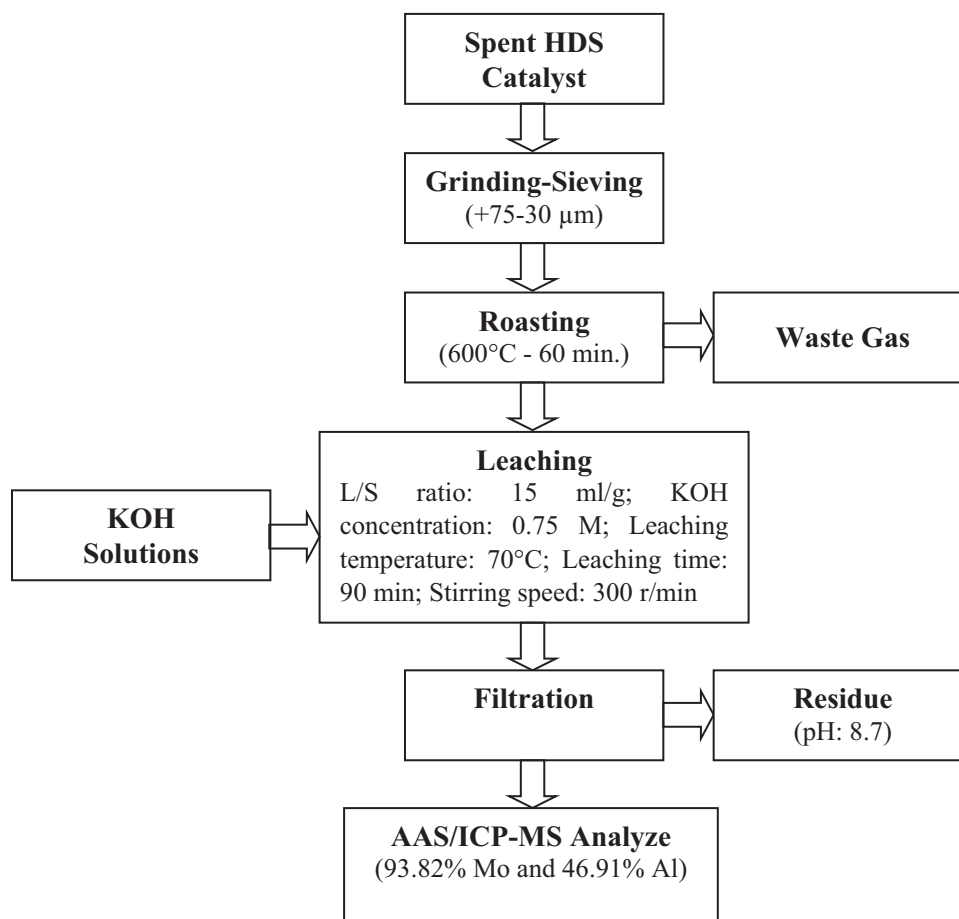


Figure 4. Flow diagram of alkali leaching process.

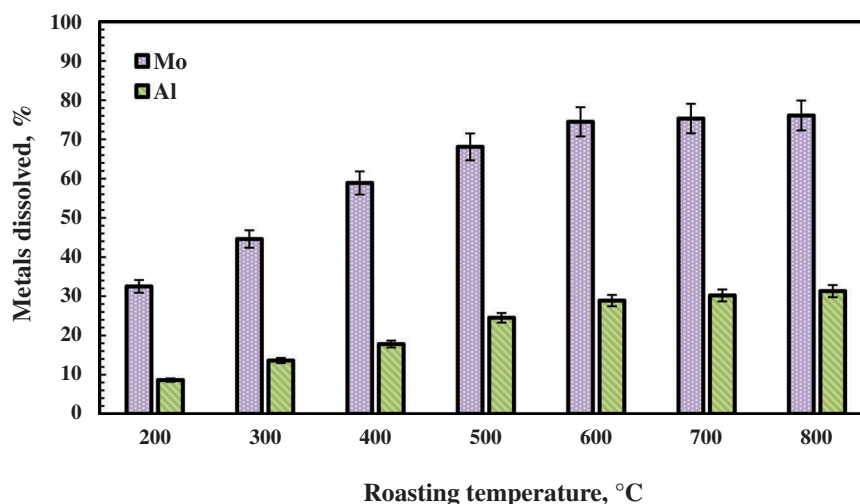


Figure 5. Effect of roasting temperature on percentage dissolution of metals [Roasting time: 45 min; particle size: +150-75 μm ; L/S ratio: 10 ml/g; KOH concentration: 1 M; leaching temperature: 80°C; leaching time: 120 min; stirring speed, 400 r/min].

Effect of KOH concentration

Different KOH concentrations (0.05–1.5 M) prepared to investigate the effect of alkali leaching agent on the recovery efficiencies of Mo and Al. As seen in Fig. 9,

the metal extraction yield improved with the increase of KOH concentration. It may be due to the presence of highly soluble Mo and Al sulfate compounds in aqueous solutions. The values of metal recovery increased

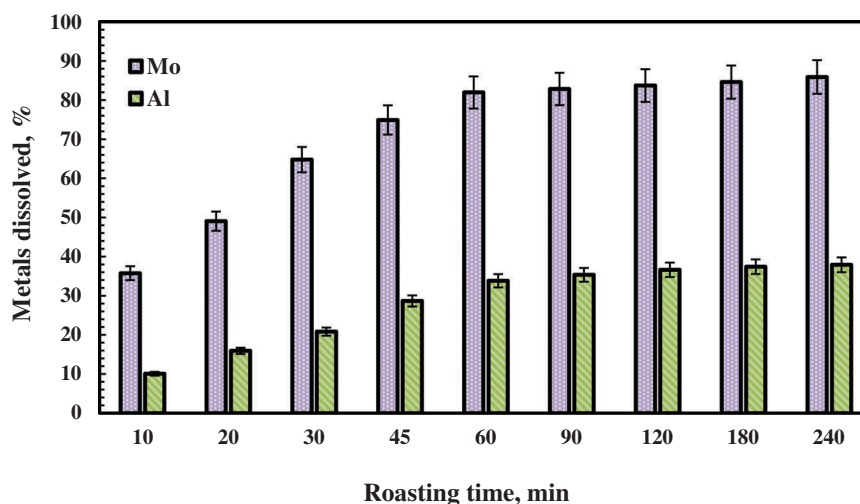


Figure 6. Effect of roasting time on percentage dissolution of metals [Roasting temperature: 600°C; particle size: +150 – 75 μm ; L/S ratio: 10 ml/g; KOH concentration: 1 M; leaching temperature: 80°C; leaching time: 120 min; stirring speed, 400 r/min].

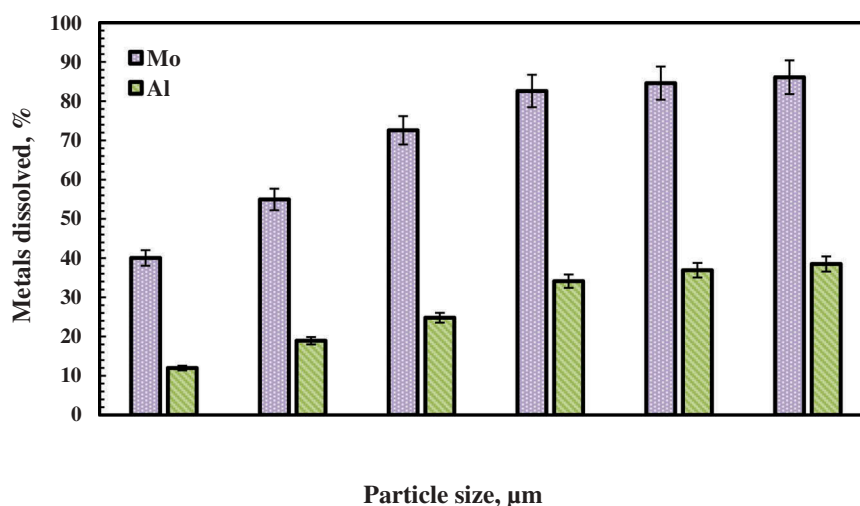


Figure 7. Effect of particle size on percentage dissolution of metals [Roasting temperature: 600°C; roasting time: 60 min; L/S ratio: 10 ml/g; KOH concentration: 1 M; leaching temperature: 80°C; leaching time: 120 min; stirring speed, 400 r/min].

steadily to 0.75 M and the leaching efficiencies for Mo and Al were found 92.66% and 41.78%, respectively. The significant increasing tendency was not observed after this concentration value. Therefore, KOH concentration (0.75 M) was chosen as the optimum alkali leaching agent concentration.

Effect of leaching temperature and time

The temperature was studied in the range from 10°C to 100°C to increase leaching efficiency and explain process kinetics. It is clearly seen from Fig. 10 that there is generally an enhancement in metal extraction values with the increase in leaching temperature. It reached 93.67% and 45.39% for Mo and Al at 70°C temperature,

respectively. There was no appreciable raise in extraction values occurred at higher leaching temperatures. As illustrated in Fig. 11, the recovery percentages of both metals increased very fast to reach approximately 92.58% (Mo) and 46.25% (Al) after 90 min. and then remained plateau after this leaching time. Thus, subsequent experiments were conducted for 90 min.

Effect of stirring speed

The stirring speed was studied in the range of 50–600 r/min. to evaluate the effect of stirring speed on Mo and Al dissolution, while all other experimental parameters are constant. In terms of presented experimental results in Fig. 12, the leaching efficiency

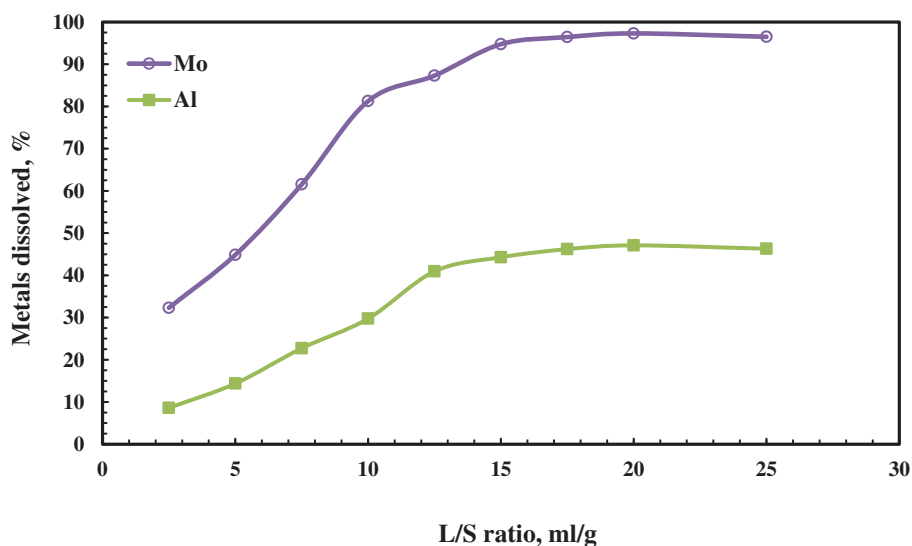


Figure 8. Effect of L/S ratio on percentage dissolution of metals [Roasting temperature: 600°C; roasting time: 60 min; particle size: +150 – 75 μm ; KOH concentration: 1 M; leaching temperature: 80°C; leaching time: 120 min; stirring speed, 400 r/min].

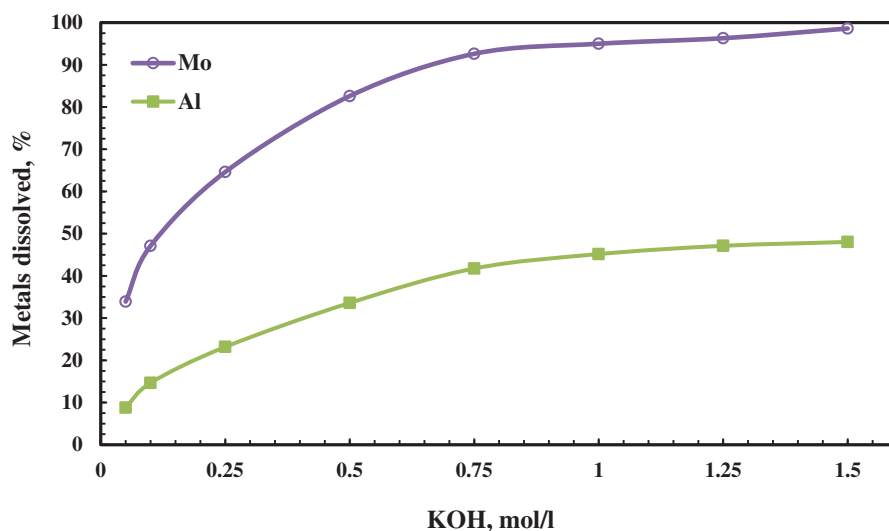


Figure 9. Effect of potassium hydroxide concentration on percentage dissolution of metals [Roasting temperature: 600°C; roasting time: 60 min; particle size: +150 – 75 μm ; L/S ratio: 15 ml/g; leaching temperature: 80°C; leaching time: 120 min; stirring speed, 400 r/min].

values of both metals (95.89% Mo and 47.95% Al) were exhibited an increasing trend toward 300 r/min and then reaching a plateau after higher stirring speed values (93.82% Mo and 46.91% Al). This may be caused that when the reactant and leaching products are diffused throughout the boundary layer, a decreasing in the boundary layer thickness around the spent HDS catalyst particles occurs and leads to a reduction in the reaction rate. Therefore, it is required that the stirring speed be chosen at a level which provides the best contact between the leaching

agent and the particle. At lower than 300 r/min, the reaction rate is likely to be controlled by a surface layer formed around the reactants and the leaching products. In the case of above 300 r/min, the dissolution rate no longer change with stirring speed indicating that the diffusion layer controls dissolution rate.^[39]

It is seen that the dissolution rate of Al (46.91%) is below 50% in optimum experimental conditions. In the literature, the production of Al from the bauxite mineral (60% Al_2O_3) is carried out at high tempera-

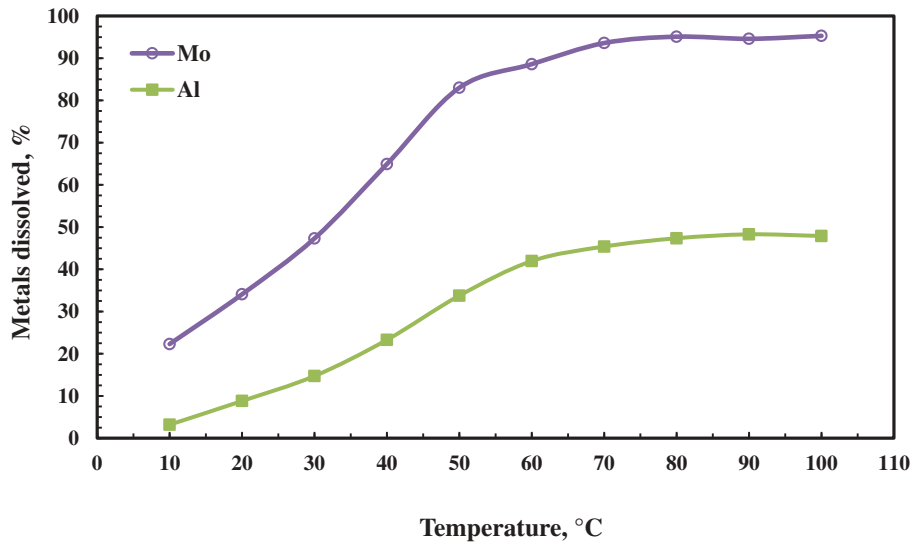


Figure 10. Effect of leaching temperature on percentage dissolution of metals [Roasting temperature: 600°C; roasting time: 60 min; particle size: +150 – 75µm; L/S ratio: 15 ml/g; KOH concentration: 0.75 M; leaching time: 120 min; stirring speed, 400 r/min].

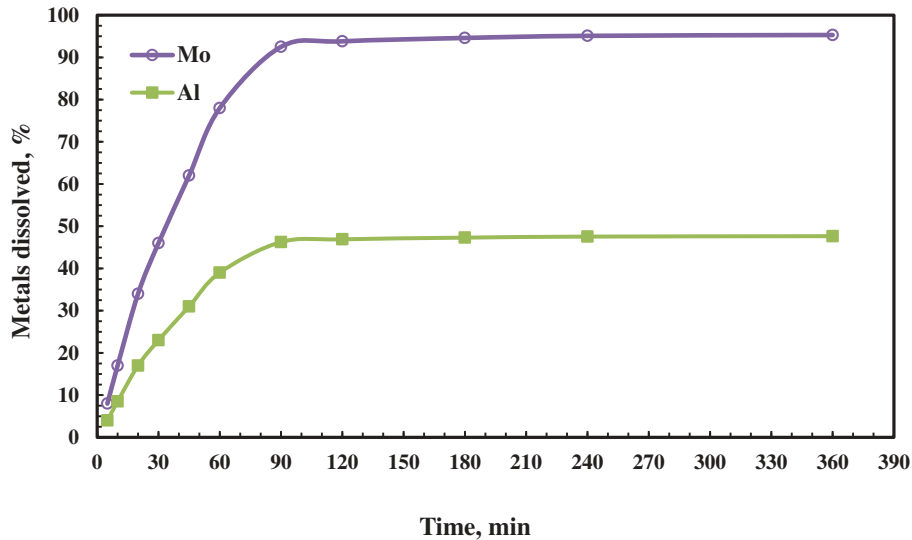


Figure 11. Effect of leaching time on percentage dissolution of metals [Roasting temperature: 600°C; roasting time: 60 min; particle size: +150 – 75 µm; L/S ratio: 15 ml/g; KOH concentration: 0.75 M; leaching temperature: 70°C; stirring speed, 400 r/min].

tures, in the presence of concentrated NaOH and in high-pressure reactors.^[40] The present study was carried out at atmospheric pressure, in the presence of low KOH concentration and at low temperatures. Therefore, it limits the amount of Al passing into the solution.

Kinetic analysis

The dissolution rates of Mo and Al metals are analyzed via shrinking core model to evaluate the leaching kinetic data. In terms of the shrinking core model, a leaching process is governed by one of the following

reaction mechanism steps; liquid film diffusion (Equation 1), or film diffusion through product layer (Equation 2) or surface chemical reaction (Equation 3). The reaction rate is controlled by the slowest step in the overall leaching reactions.^[41,42] The above aforementioned equations are presented below;

$$t = k[1 - (1 - x)] \quad (1)$$

$$t = k[1 - 3(1 - x)^{2/3} + 2(1 - x)] \quad (2)$$

$$t = k[1 - (1 - x)^{1/3}] \quad (3)$$

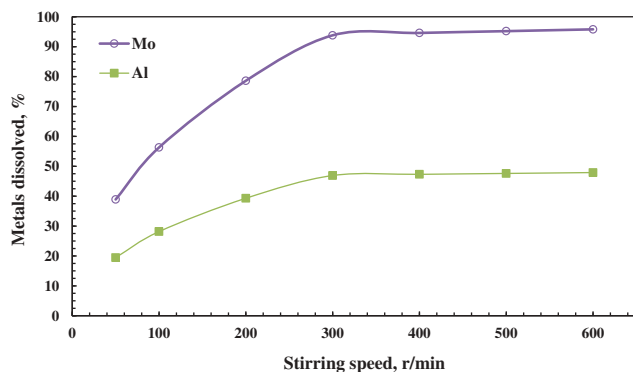


Figure 12. Effect of stirring speed on percentage dissolution of metals [Roasting temperature: 600°C; roasting time: 60 min; particle size: +150 – 75 µm; L/S ratio: 15 ml/g; KOH concentration: 0.75 M; leaching temperature: 70°C; leaching time: 90 min].

x is the dissolved amount of metal, t is the reaction time (min.) and k is the reaction rate constant (min^{-1}). A graph of the left side of the above equations vs. time t is plotted and the reaction rate constants for each mechanism are calculated from the slope of the graph. Similarly, the correlation coefficients (R^2) at different temperatures for both metals (Mo and Al) were calculated using the same equations. As illustrated in Table 3, the kinetic data of Mo and Al are good compatible to the liquid film diffusion mechanism because of very high R^2 values (>0.99) in all temperatures.

The change of reaction rate constant with temperature was calculated by Arrhenius equation (Equation 4);

$$k = A.e^{-E_a/RT} \quad (4)$$

E_a is the activation energy (J/mol), k is the reaction rate constant (min^{-1}), A is the frequency factor, R is the universal gas constant (8.314 J/mol.K) and T is the temperature (K).

The magnitude of the activation energy (E_a) is account for whether a heterogeneous reaction mechanism is controlled by surface chemical reactions ($E_a > 40$ kJ/mol) or film diffusion ($E_a < 20$ kJ/mol).^[41–43] As shown in Fig. 13, E_a values of both metals were calculated from the slope of $\ln k$ plotted against $1/T$ and found to be 14.71 kJ/mol and 17.84 kJ/mol for Mo and Al, respectively. In the light of these findings, it is slightly indicated that the leaching process of Mo and Al metals is governed by the liquid film diffusion mechanism.

Conclusions

In present study, the leaching process parameters were optimized to recovery precious metals from the spent HDS catalyst using KOH leaching solution. However,

Table 3. The best-fit equations and correlation coefficient values (R^2) for alkali leaching process.

Metals	Kinetic Models	Temperature, °C									
		20	30	40	50	60	70	80	90		
Mo	Liquid film diffusion control	$R^2 = 0.9913$	$R^2 = 0.9959$	$R^2 = 0.9908$	$R^2 = 0.9852$	$R^2 = 0.9912$	$R^2 = 0.9952$	$R^2 = 0.9945$	$R^2 = 0.9906$		
	Surface chemical reaction control	$y = 0.0011-0.023$	$y = 0.0015-0.038$	$y = 0.0019-0.049$	$y = 0.0022-0.054$	$y = 0.0025-0.074$	$y = 0.0029-0.085$	$y = 0.0032-0.089$	$y = 0.0038-0.097$		
	Film diffusion control through product layer	$R^2 = 0.9636$	$R^2 = 0.9814$	$R^2 = 0.9852$	$R^2 = 0.9892$	$R^2 = 0.9885$	$R^2 = 0.9902$	$R^2 = 0.9832$	$R^2 = 0.9909$		
Al	Liquid film diffusion control	$y = 0.0071-0.021$	$y = 0.0087-0.034$	$y = 0.0057-0.098$	$y = 0.0065-0.075$	$y = 0.0091-0.021$	$y = 0.0099-0.014$	$y = 0.0117-0.008$	$y = 0.0105-0.085$		
	Surface chemical reaction control	$R^2 = 0.9916$	$R^2 = 0.9859$	$R^2 = 0.9894$	$R^2 = 0.9809$	$R^2 = 0.9902$	$R^2 = 0.9815$	$R^2 = 0.9899$	$R^2 = 0.9885$		
	Film diffusion control through product layer	$y = 0.036-0.109$	$y = 0.045-0.104$	$y = 0.058-0.184$	$y = 0.067-0.162$	$y = 0.086-0.149$	$y = 0.092-0.124$	$y = 0.081-0.134$	$y = 0.099-0.112$		
		$R^2 = 0.9900$	$R^2 = 0.9994$	$R^2 = 0.9952$	$R^2 = 0.9914$	$R^2 = 0.9920$	$R^2 = 0.9901$	$R^2 = 0.9932$	$R^2 = 0.9987$		
		$y = 0.0017-0.015$	$y = 0.0023-0.031$	$y = 0.003-0.058$	$y = 0.0036-0.069$	$y = 0.0048-0.074$	$y = 0.0055-0.089$	$y = 0.0061-0.098$	$y = 0.0069-0.112$		
		$R^2 = 0.9809$	$R^2 = 0.9885$	$R^2 = 0.9855$	$R^2 = 0.9899$	$R^2 = 0.9842$	$R^2 = 0.9900$	$R^2 = 0.9872$	$R^2 = 0.9952$		
		$y = 0.0044-0.048$	$y = 0.005-0.081$	$y = 0.0065-0.033$	$y = 0.0071-0.082$	$y = 0.0054-0.048$	$y = 0.0081-0.081$	$y = 0.0075-0.033$	$y = 0.0089-0.082$		
		$R^2 = 0.9756$	$R^2 = 0.9745$	$R^2 = 0.9805$	$R^2 = 0.9843$	$R^2 = 0.9894$	$R^2 = 0.9723$	$R^2 = 0.9998$	$R^2 = 0.9852$		
		$y = 0.051-0.111$	$y = 0.065-0.123$	$y = 0.076-0.149$	$y = 0.083-0.169$	$y = 0.091-0.151$	$y = 0.105-0.193$	$y = 0.116-0.249$	$y = 0.123-0.389$		

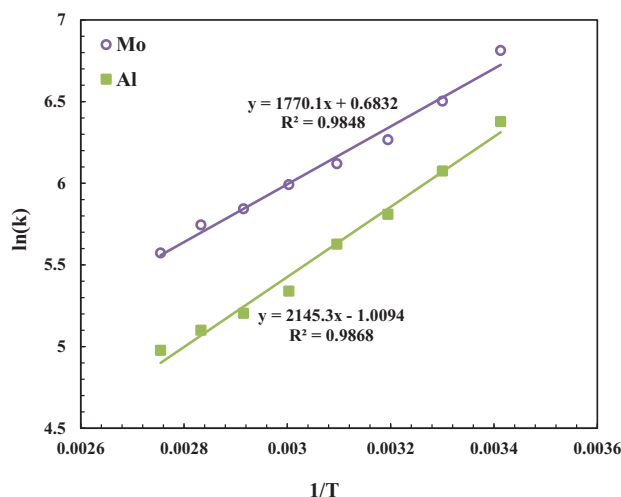


Figure 13. Arrhenius plot of $\ln(k)$ versus $1/T$.

the dissolved efficiencies of Mo and Al were only examined due to the low solubility of metal oxides of Ni and Co in the presence of alkali leaching agent. The highest extraction yields (93.82% Mo and 46.91% Al) were obtained under optimum experimental conditions; roasting temperature of 600°C, roasting time of 60 min, particle size of +150-75 μm , L/S ratio of 15 ml/g, KOH concentration of 0.75 M, leaching temperature of 70°C, leaching time of 90 min. and stirring speed of 300 r/min. The leaching behaviors of Al and Mo are represented by the shrinking core model and the overall leaching process is controlled by liquid film diffusion. E_a values found to be 14.71 kJ/mol and 17.84 kJ/mol for Mo and Al, respectively.

Highlights

The leaching behaviors of Mo and Al were studied in the presence of alkali leaching agent.

83.54% and 36.89% of Mo and Al were recovered under optimum leaching conditions.

The shrinking core model is represented the leaching process and the overall leaching process is controlled by liquid film diffusion.

The values of activation energy (E_a) of Mo and Al calculated to be 14.71 and 17.84 kJ/mol, respectively.

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